Water Quality Technical Note PD-04
July 1999

WQTS

Sorption Characteristics of Sediments in the Upper Mississippi River System Above Lake Pepin

by W. F. James, J. W. Barko, and H. L. Eakin

PURPOSE: This technical note examines equilibrium phosphorus processes and sorption characteristics for sediments collected from the Minnesota River, immediately upstream from its confluence with the Upper Mississippi River (UMR), and from Lake Pepin of the UMR, located approximately 70 miles downstream of the Minnesota River inflow.

BACKGROUND: Suspended sediments can play an important role in the regulation of nutrient dynamics and primary productivity in aquatic systems by influencing nutrient concentrations in the water column through equilibrium processes (adsorption-desorption) between solid and aqueous phases (Meyer 1979, Mayer and Gloss 1980, Froelich 1988). In particular, adsorption-desorption reactions may be the primary means of controlling phosphorus (P) concentrations in the water column for water bodies receiving high suspended sediment loadings via the watershed. Since phosphorus is generally an important nutrient for phytoplankton growth in freshwater systems, there is a need to examine and understand phosphorus equilibrium processes and fluxes in relation to soluble phosphorus concentrations and overall primary productivity. Very little information exists that links watershed-derived suspended sediment transport to phosphorus adsorption/desorption processes and to the regulation of soluble phosphorus concentrations in aquatic systems.

Lake Pepin, a natural impoundment in the Upper Mississippi River (UMR), receives excessive phosphorus loading from the agriculturally-dominated Minnesota River basin and the Metropolitan Wastewater Treatment Plant (Metro Plant), which both discharge into the Mississippi River approximately 50 miles upstream of Lake Pepin. James, Barko, and Eakin (in preparation) determined that phosphorus transformations between particulate and soluble phases (adsorption-desorption processes) may be an important mechanism in the phosphorus economy of Lake Pepin. This information is expanded by examining the importance of suspended sediment transport through the UMR in regulating phosphorus dynamics above Lake Pepin via adsorption-desorption processes. This note specifically examines differences in phosphorus equilibrium processes for sediments collected in the Minnesota River and in Lake Pepin.

METHODS: The reach of the UMR examined in this study included Pools 2, 3, and 4 of the U.S. Army Corps of Engineers lock and dam system. Lake Pepin is included as part of Pool 4 of the UMR (Figure 1) and receives inflows from a 122,000-km^2 watershed (Minnesota Pollution Control Agency 1993). Major tributary inputs to the UMR and Lake Pepin are the Mississippi, Minnesota, and St. Croix Rivers. The Minnesota River discharges into Pool 2 and the St. Croix River discharges into Pool 3 of the UMR. The Metropolitan Wastewater Treatment Plant (Metro Plant), located in St. Paul, MN, discharges high concentrations of phosphorus into Pool 2 approximately 12 miles downstream of the Minnesota River inflow. The Minnesota River dominates suspended sediment loading to the UMR, while the Metro Plant contributes up to 50 percent of the soluble phosphorus load to the UMR (James, Barko, and Eakin (in preparation)).

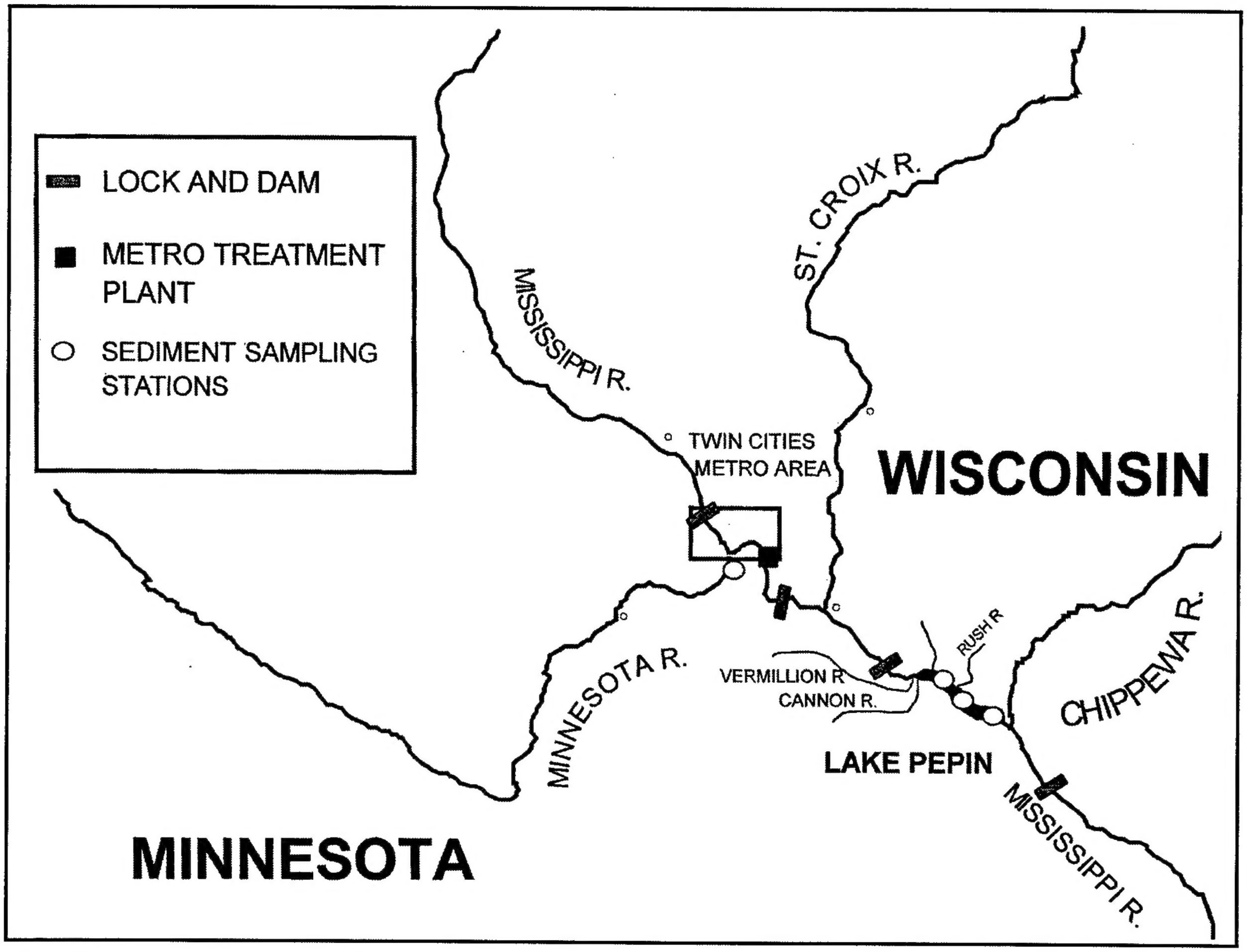

Figure 1. Sediment sampling stations in the Upper Mississippi River system

Three surface sediment samples (upper 1 cm) were collected from the Minnesota River near Ft. Snelling, MN, and surface sediment samples were collected at river miles 766, 775, and 781 of Lake Pepin in late 1997 to early 1998 to characterize phosphorus sorption/desorption characteristics (Figure 1). Stations in Lake Pepin were treated as triplicates for analysis of sorption characteristics. The sediments were gently homogenized and centrifuged at ~2,500 rpm for 10 min to remove excess pore water. Sediment aliquots (~500 mg/L dry weight equivalent) from each location were subjected to a series of soluble reactive phosphorus (KH_2PO_4 as SRP) standards ranging from 0 to 0.5 mg/L (i.e., 0, 0.125, 0.250, and 0.500 mg/L) for examination of adsorption and desorption over a 24-hr period. The concentration of suspended sediment used in the study fell within the range of concentrations occurring naturally in the UMR during periods of elevated inflow (James, Barko, and Eakin 1997). Surface water from Eau Galle Reservoir, WI, was used as the lake water medium because it was phosphate-free and exhibited cationic strength, conductivity, and pH very similar to that of surface water in Lake Pepin. Chloroform (0.1 percent) was added to inhibit biological activity. The sediment systems, containing sediment, lake water, and known concentrations of SRP, were shaken uniformly for 24 hr, then sampled and analyzed for SRP (American Public Health Association (APHA) 1992). The sediment systems were maintained under oxic conditions at a pH of approximately 8.0 to 8.3 and a temperature of approximately 20 °C to simulate conditions in the UMR during the summer period.

Adsorption and desorption were calculated as the change in SRP (i.e., SRP at 0 hr minus SRP at 24 hr) normalized with respect to sediment dry mass (i.e., mg SRP/g dry mass) and plotted as a function of final SRP concentration (Froelich 1988). The equilibrium phosphate concentration (EPC, mg/L) was calculated as the concentration where net sorption was zero (i.e., often called the crossover point (Mayer and Gloss 1980)). The linear adsorption coefficient (LAC, L/g) was calculated as the linear slope near the EPC. The native adsorbed phosphate (NAP, mg/g sediment) was calculated as

$$NAP = (LAC)(EPC) \tag{1}$$

In a separate experiment, sediments from the Minnesota River were pretreated with a solution of high SRP (as KH_2PO_4) before conducting the adsorption-desorption experiments, in order to simulate conditions of high SRP concentrations that occur in Pool 2, due to discharges from the Metro Plant. Minnesota River sediments (concentration = 500 mg dry mass/L) were exposed to a solution of filtered Eau Galle Lake water containing 0.2 mg/L phosphorus (as KH_2PO_4) for a 3-day period. This concentration fell within the range of concentrations that occur in Pool 2 (James, Barko, and Eakin 1997). The sediment contained in the P-rich solution was recovered via decantation and centrifugation after the treatment period and then subjected to the same series of SRP standards as described above for other sediments for determination of adsorption-desorption characteristics.

RESULTS AND DISCUSSION: Marked differences in sorption characteristics (Figure 2) and in NAP and EPC concentrations (Table 1) were observed between Minnesota River and Lake Pepin sediments. Minnesota River sediments had a significantly (p 0.05) lower NAP and EPC than Lake Pepin sediments (Table 1). Thus, phosphorus desorption was minor and occurred only when ambient SRP concentrations were near zero. At concentrations exceeding the EPC, phosphorus adsorption increased linearly with increasing ambient SRP concentration for sediments collected from the Minnesota River. In contrast, EPC and NAP for sediments from Lake Pepin were very high (Table 1) compared to aquatic sediments examined in other systems (Meyer 1979; Mayer and Gloss 1980; studies cited in Froelich (1988); Olila and Reddy 1993), indicating a strong potential for equilibrium influences on phosphorus concentrations in the water column when ambient phosphorus concentrations fall below the EPC.

EPC and NAP for sediments collected from Lake Pepin were also significantly ($p < 0.05$) greater than those values determined for Minnesota River sediment (Table 1). Phosphorus desorption was also much more substantial for Lake Pepin than Minnesota River sediments at ambient SRP concentrations less than 0.125 mg/L (Figure 2). In contrast, phosphorus adsorption was much less ($p < 0.05$) for Lake Pepin than Minnesota River sediments at SRP concentrations greater than 0.25 mg/L, suggesting a lower capacity to adsorb phosphorus (i.e., less available binding sites) at high ambient phosphorus (i.e., ambient phosphorus > EPC) for sediments transported into Lake Pepin.

One mechanism that could cause changes in phosphorus sorption characteristics and increases in the NAP and EPC of Minnesota River sediment as it is transported through Pools 2 and 3 to Lake Pepin is a change in phosphorus equilibrium (i.e., ambient phosphorus > EPC) in the water column and adsorption of phosphorus onto transported sediment. Simulated changes in phosphorus equilibrium via preconditioning Minnesota River sediment with an elevated phosphate concentration over a 3-day period resulted in a significant increase in the NAP and EPC of the sediment over those

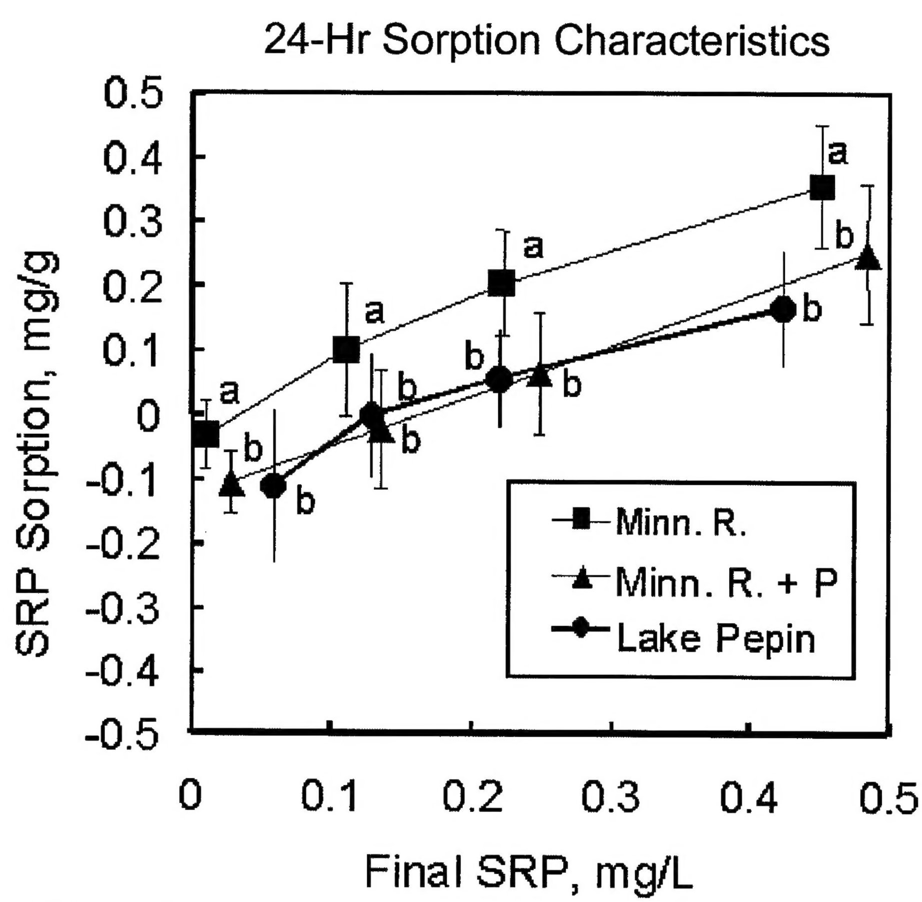

Figure 2. Adsorption or desorption of phosphorus as a function of final SRP equilibrium concentration for sediments collected from the Minnesota River (Minn. R.) and Lake Pepin. Negative SRP sorption indicates desorption of phosphorus from sediments while a positive value indicates adsorption of phosphorus onto sediments. Minn R. + phosphorus represents Minnesota River sediments pretreated with 0.2 mg/L phosphorus as KH_2PO_4 over a 3-day period. This phosphorus preconditioning procedure promoted phosphorus adsorption onto the sediment, simulating potential conditions that occur when Minnesota River sediment transported through Pool 2 of the UMR is exposed to high SRP originating from the Metro Plant. Different letters indicate significant differences at the 5-percent level or less, based on ANOVA (Duncan-Waller; Statistical Analysis System (SAS) 1994)

values observed for Minnesota River sediment with no prior phosphorus preconditioning (Table 1). In addition, the phosphorus adsorption capacity declined at higher phosphorus concentrations as a result of phosphorus preconditioning, suggesting that there were fewer binding sites available for phosphorus adsorption as a result of phosphorus preconditioning.

Results indicate that Minnesota River suspended sediment is capable of adsorbing phosphorus and filling binding sites as it passes through the UMR. A prominent source of SRP that could drive a change in phosphorus equilibrium and phosphorus adsorption onto sediment is the Metro Plant discharge into Pool 2 of the UMR (Figure 1). Concentrations of SRP in this region typically increase from < 0.060 mg/L upstream of the Metro Plant to > 0.120 mg/L in the vicinity of the plant (James,

Table 1
Means (± 1 S.E.) for Native Adsorbed Phosphorus at Equilibrium and the Equilibrium Phosphate Concentration (EPC) for Sediments Collected from the Minnesota River and Lake Pepin*

Sediment	Native Adsorbed phosphorus (mg/g)	EPC (mg/L)
Minnesota River	0.043[a] (0.006)	0.038[a] (0.003)
Lake Pepin	0.178[b] (0.058)	0.162[b] (0.018)
Minnesota River after phosphorus-preconditioning over a 3-day period	0.126[b] (0.004)	0.164[b] (0.015)

* The last row of the table shows results for Minnesota River sediments that were subjected to a solution of lake water containing a phosphorus concentration of 0.2 mg/L over a 3-day period (phosphorus-preconditioning) prior to running adsorption-desorption experiments. This procedure promoted phosphorus adsorption onto the sediment, simulating potential conditions that occur when Minnesota River sediment transported through Pool 2 of the UMR is exposed to high SRP originating from the Metro Plant. Different letters indicate significant differences at the 5-percent level or less, based on ANOVA of logarithmically transformed data (Duncan-Waller; SAS 1994).

Barko, and Eakin, in preparation). Thus, phosphorus inputs in this region are driving aqueous phosphorus concentrations above the EPC of 0.038 mg/L for Minnesota River sediment, which favors phosphorus adsorption onto sediment.

The implications of elevated NAP and EPC of Minnesota River sediment as a result of phosphorus-preconditioning are enhanced desorption potential downstream if ambient SRP declines below the EPC. Dilution of SRP below the EPC in Pool 3 by the St. Croix River, located 10 miles upstream of Lake Pepin, provides a mechanism for phosphorus desorption from Minnesota River sediments at downstream locations and must be considered in the phosphorus economy of Lake Pepin.

ACKNOWLEDGMENTS: The authors gratefully acknowledge Mses. Susan Fox, Michele Huppert, Brenda Lamb, and Holly Wallace, and Mr. Dale Dressel of the Eau Galle Aquatic Ecology Laboratory, WES, Spring Valley, WI, for water and sediment sampling, chemical analysis, and the execution of studies on phosphorus adsorption-desorption processes.

POINTS OF CONTACT: This technical note was written by Messrs. William F. James and Harry L. Eakin of the U.S. Army Engineer Waterways Experiment Station Eau Galle Aquatic Ecology Laboratory, and Dr. John W. Barko of the U.S. Army Engineer Waterways Experiment Station. For additional information, contact Mr. James (715-778-5896, *jamesw1@sin.bright.net*) or the managers of the Water Quality Research Program, Dr. Barko (601-634-3654, *barkoj @wes.army.mil*) or Mr. Robert C. Gunkel (601-634-3722, *gunkelr@wes.army.mil*). This technical note should be cited as follows:

> James, W. F., Barko, J. W., and Eakin, H. L. (1999). "Sorption characteristics of sediments in the Upper Mississippi River System above Lake Pepin," *Water Quality Technical Notes Collection* (WQTN PD-04), U.S. Army Engineer Research and Development Center, Vicksburg, MS. *www.wes.army.mil/el/elpubs/wqtncont.html*

REFERENCES

American Public Health Association. (1992). *Standard methods for the examination of water and wastewater.* 18th ed.

Froelich, P. N. (1988). "Kinetic control of dissolved phosphate in natural rivers and estuaries: A primer on the phosphate buffer mechanism," *Limnol. Oceanogr.* 33, 49-668.

James, W. F., Barko, J. W., and Eakin, H. L. (1997). "Analysis of nutrient/seston fluxes and phytoplankton dynamics in Lake Pepin (Upper Mississippi River) 1996. Third Interim Report," Report submitted to the Metropolitan Council, St. Paul, MN.

James, W. F., Barko, J. W., and Eakin, H. L. "Diffusive and kinetic fluxes of phosphorus from sediments in relation to phosphorus dynamics in Lake Pepin, Upper Mississippi River," in preparation, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

Mayer, L. M., and Gloss, S. P. (1980). "Buffering of silica and phosphate in a turbid river," *Limnol. Oceanogr.* 25, 12-25.

Meyer, J. L. (1979). "The role of sediments and bryophytes in phosphorus dynamics in a headwater stream ecosystem," *Limnol. Oceanogr.* 24, 365-375.

Minnesota Pollution Control Agency. (1993). "Mississippi River phosphorus study, Section 3: Lake Pepin water quality: 1976-1991," Minnesota Pollution Control Agency, Water Quality Division, St. Paul, MN.

Olila, O. G., and Reddy, K. R. (1993). "Phosphorus sorption characteristics of sediments in shallow eutrophic lakes of Florida," *Arch. Hydrobiol.* 129, 45-65.

Statistical Analysis System. (1994). "SAS/STAT User's Guide, Version 6," SAS Institute, Cary, NC.